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(54) **Thickening agent which modifies the rheological characteristics of charged and/or pigmented, white or colored aqueous compositions**

(57) Associative thickening copolymer water-soluble in a neutral or alkaline medium, for charged and/or pigmented, white or colored aqueous compositions, composed

- a) of at least one ethylenically unsaturated monomer having at least one carboxylic function,
- b) of at least one other ethylenically unsaturated monomer devoid of carboxylic function.
- c) of at least one surfactant monomer having at least one urethane function resulting from the reaction of an ethylenically unsaturated isocyanate with a surfactant compound, having a hydroxyl function that is reactive towards the  $-NCO$  group,

characterized in that said copolymer belongs to the group consisting of those which, by definition, when placed in an aqueous solution containing 2 % by weight of dry matter and brought to pH 9 by the addition of ammonia, at a temperature of 20 °C, have a Brookfield viscosity at 100 rpm of at most equal to 220 centipoises.

The copolymer according to the invention is used in charged and/or pigmented aqueous compositions such as coating compositions, and more particularly in paints, coating slips, printing pastes, leather finishing products, compositions for cosmetics and detergents, and drilling fluids.

**Description**

**Thickening agent which modifies the rheological characteristics of charged and/or pigmented, white or colored aqueous compositions**

Field of the invention

The invention relates to an associative thickening copolymer that is water-soluble in a neutral or alkaline medium, and has the property of modifying the rheological characteristics of charged and/or pigmented, white or colored aqueous compositions.

The invention also relates to charged and/or pigmented, white or colored aqueous compositions for which it is desirable that they have a Newtonian behavior and which contain said associative thickening copolymer whose effect on the medium simultaneously provides a good rheological compromise at high and low shearing stress, which is reflected by good covering and film tension characteristics after application, while retaining good resistance to running.

In the description of the subject of the invention, the expression "charged and/or pigmented, white or colored aqueous compositions" defines the field of aqueous compositions of charges and/or pigments such as coating compositions and, more particularly, paints, coating slips, printing pastes, leather finishing products, compositions for cosmetics and detergents, and drilling fluids.

Moreover, and more particularly in the case of paints, "covering power" characterizes the quantity of paint deposited per unit surface area, "resistance to running" defines the ability of a paint to resist running after its application to a substrate to be protected. and

finally “film tension” after application defines the ability of said paint to even out the thickness irregularities resulting from its application on a substrate to be protected.

### Background of the invention

For a person skilled in the art, a charged and/or pigmented aqueous composition is formed from a liquid phase which may be water or an organic water-miscible solvent, or even a mixture of these two, from a polymer in emulsion in the liquid phase which is called “binder”, from charges and/or pigments, from an agent which disperses the charges and/or pigments which can be a water-soluble polymer or copolymer, from adjuvants as varied as coalescence agents, biocides, antifoaming agents or others, and finally from a thickening agent which is a natural or synthetic polymer or copolymer.

For a long time it was found during use that the presence of a thickening agent in a charged and/or pigmented aqueous composition was necessary in order to modify its rheological characteristics.

Several species of thickening agents for charged and/or pigmented aqueous compositions have already been proposed to persons skilled in the art and have been abundantly described in the specialized literature.

A first species of thickening agents for charged and/or pigmented aqueous compositions consists of cellulose derivatives which have the property of viscosifying only the aqueous phase of said compositions.

However, the field of application of this first species of thickening agents is a limited one, because disadvantages occur, causing problems to the user, disadvantages such as difficulties of dissolution in the aqueous media, an often slow hydration kinetics, high sensitivity to bacteria, and also an inability to develop, and more specifically, to adjust *a posteriori*, the viscosity of the charged and/or pigmented aqueous compositions.

Thus it seems that this first species of thickening agents causes, within charged and/or pigmented aqueous compositions in which it is used, pseudo-plastic rheological characteristics which could be troublesome, such as a high viscosity in the absence of mechanical stress but which decreases to a very great extent under the effect of shearing stress, resulting in a poor covering power.

Another species of thickening agents has been proposed for overcoming the aforementioned drawbacks of this first species. This other species is formed from synthetic latexes which may be acrylic, illustrative descriptions of which are given e. g. in patents such as French Patent 2,131,128, French Patent 2,281, 389. U. S. Patent 2,798,053, U. S. Patent 2,985,625 or even U. S. Patent 2,958,679.

Thus, a description is given (French Patent 2,281,389) of a cross-linked polymer of maleic anhydride and ethylene in the presence of trialkyl isocyanurate, which can be used as thickening agent for aqueous systems such as synthetic latex-based paints, for the flocculation treatment of ores, and for coagulation treatment of industrial or domestic water.

These thickening agents are generally polymers of carboxylic acids having an ethylenic function, or copolymers of these same acids and their esters present in the form a low-viscosity aqueous emulsion of the oil in water type.

These thickening agents, which are soluble in aqueous and alkaline media, have the advantage over the above-mentioned cellulose derivatives of being more easily used and of being insensitive to bacterial attack.

However, as the first species of thickening agents, the second species has certain drawbacks such as causing the thickening of only the aqueous phase of said compositions, or even of providing these compositions with highly pseudo-plastic rheological characteristics which are not suitable for all paint formulations.

More recently a last species of water-soluble thickening agents has appeared in the field of charged and/or pigmented aqueous compositions, thickening agents traditionally called associative thickening agents, because they act not only by increasing the viscosity of the aqueous phase (by solubilization) but also by creating various bonds between the copolymer and certain constituents of the compositions, most likely through the appearance of hydrophobic interactions and hydrogen bonds. The advantage of these associative thickening agents over the aforementioned agents is to provide the charged and/or pigmented compositions in which they are used with a less pseudo-plastic behavior.

In particular, in the case of certain paints, a person skilled in the art seeks to obtain a viscosity under low shear stress which is sufficiently low so that the film deposited on the substrate to be protected has a tendency to level out well the thickness irregularities caused by the application (appropriate film tension), and has a viscosity under high shear which is sufficiently high for improving the covering power and for decreasing the projections when said paints are applied by means of a roller.

This last species of associative thickening agents has developed into two families, that of polyurethane associative thickening agents and that of acrylic associative thickening agents.

The polyurethane associative thickening agents which belong to the first family possess, in their molecule, one or more polyether chains terminating with hydrophobic groups such as e.g. alkyls, aryls, alkylaryls, and are obtained by condensation chemistry.

Such agents are described in many patents, e. g. in British Patent 1,069,735, U. S. Patent 3,770,684, U. S. Patent 4,079,028 and U. S. Patent 4,155,892.

But, although these agents provide the charged and/or pigmented compositions in which they are used with desirable rheological characteristics, they are the source of certain troublesome disadvantages for their user.

In effect, these agents are present in a viscous form which is not easy to handle, possibly in solution in mixtures of water and solvent(s), and the solvent may be more or less toxic and thus these agents may be of limited use, or even have reactive incompatibilities with certain constituents of the charged and/or pigmented compositions.

The acrylic associative thickening agents obtained by radical polymerization, belonging to the second family and water-soluble in a neutral or alkaline medium, are formed from copolymers generally prepared from ethylenic carboxylic acids, possibly of esters of these acids and/or other monomers, and finally from at least one particular functional monomer having a side chain composed of polyether groups possessing hydrophobic hydrocarbon terminal groups.

The nature of the particular functional monomer has been found to be a determining factor in the rheological behavior of the charged and/or pigmented compositions containing the corresponding thickening agent.

Thus, the particular functional monomer may be an acrylate or methacrylate of a surfactant alcohol (European Patent 0 013 836 and U. S. Patent 4,384,096) or it may result from the esterification by a surfactant alcohol of acrylic acid oligomers (U. S. Patent 4,421,902). This particular functional polymer may also be an oxyethylated ester of crotonic acid (U. S. Patent 4,569,965) or even a half ester of maleic anhydride (European Patent 0 248 612) or a surfactant ether of allyl alcohol (European Patent 0 216 479).

Finally, this particular functional monomer can result from the condensation of a surfactant alcohol and an unsaturated isocyanate (U. S. Patents 4,514,552 and 4,600,761), the presence of O-C(O)-NH- urethane groups on the side chains of the copolymer producing a beneficial effect on the rheological behavior of the charged and/or pigmented aqueous compositions and particularly of the aqueous paints.

The object sought by the use of the acrylic associative thickening agents was to modify, in the most favorable manner, the rheological characteristics of said compositions by their presence, so that they preferably have a controlled viscosity simultaneously under high and low shearing stresses, so as to have a good covering power, an acceptable resistance to running and an appropriate film tension.

Now, it has been noted that among the many prior-art associative acrylic thickening agents

- some already had an acceptable rheological profile, but at the price of high amounts of use which the formulator wanted to see decreased,
- others, such as those mentioned in U. S. Patent 4,514,552, did not manage to control simultaneously the viscosities at high and low shearing stresses..

#### Summary of the invention

In view of the aforementioned drawbacks, the Applicant, in carrying out his studies, has found and perfected an associative thickening copolymer which is water-soluble in a neutral or alkaline medium and, unlike the prior art, provides the charged and/or pigmented aqueous compositions with a good state of rheological compromise at high and low shearing stresses which is reflected by a high covering power and a good film tension while retaining an excellent resistance to running, both for white and colored compositions, and which uses lower quantities.

According to the invention the associative thickening copolymer water-soluble in a neutral or alkaline medium and composed

- a) of at least one ethylenically unsaturated monomer having at least one carboxylic function,
- b) of at least one other ethylenically unsaturated monomer devoid of carboxylic function.
- c) of at least one surfactant monomer having at least one urethane function resulting from the reaction of an ethylenically unsaturated isocyanate with a surfactant compound, having a hydroxyl function that is reactive towards the  $\text{-NCO}$  group,

is characterized in that said copolymer belongs to the group consisting of those which, by definition, when placed in an aqueous solution containing 2 % by weight of dry matter and brought to pH 9 by the addition of ammonia, at a temperature of 20 °C, have a Brookfield RVT viscosity at 100 rpm of at most equal to 220 centipoises.

#### Detailed description

The associative thickening copolymer according to the invention is distinguished from the prior art in that it provides a state of compromise in said compositions and paints, leading to a balance between the extreme effects previously observed.

In other words, the associative thickening copolymer of the invention, when used in charged and/or pigmented aqueous compositions, generates media whose general rheological characteristics approach a Newtonian behavior, media whose viscosity under high shearing stress is increased and whose viscosity under low shearing stress is decreased in relation to the prior art, thereby improving the covering power and film tension characteristics after application, while maintaining a good resistance to running,

The Newtonian behavior of the aqueous compositions containing the associative thickening copolymer according to the invention is acquired jointly as a result of the

incorporation, in its structure, of a surfactant monomer having at least one urethane function, and the fact that the molecular weight of said copolymer is very low, said molecular weight being expressed by measurement of the mobile 1 to 3 RVT Brookfield viscosity at 100 rpm of an aqueous solution containing 2 % by weight of said dry copolymer brought to a pH of 9 by the addition of ammonia and at a temperature of 20 °C, the upper limit of the Brookfield viscosity measured under these conditions being 220 centipoises at the most.

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Apart from this conditional field of Brookfield viscosities as indicated above, any copolymer of the same structure but generating a viscosity of more than 220 centipoises under the conditions indicated for this measurement leads to aqueous compositions having perturbed, even bad, rheological characteristics when used as a thickening agent, more precisely in the case of gloss or semigloss paints.

Thus, as Applicant was able to note, it appeared in a surprising manner that the two above-mentioned conditions leading to the copolymer according to the invention fully cooperate, by the selection of low molecular weights, in creating a state of synergy which makes it possible to obtain charged and/or pigmented, white or colored aqueous compositions having rheological characteristics which approach a Newtonian behavior.

The associative thickening copolymer according to the invention is composed, as already stated above, of at least three types of monomers.

The first type of monomer, which is an ethylenically unsaturated carboxylic acid, is a compound having an ethylenic bond and at least one carboxyl group or a carboxylic acid anhydride group.

The carboxylated ethylenic monomer may be selected from among monoacids, such as acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid, cinnamic acid; diacids such as itaconic acid, fumaric acid, maleic acid, citraconic acid; anhydrides of carboxylic

acids such as maleic anhydride; and half esters of diacids such as the C<sub>1</sub> to C<sub>4</sub> monoesters of maleic acid or itaconic acid.

However, the carboxylated ethylenic monomer is preferably selected from the group consisting of acrylic acid, methacrylic acid and itaconic acid.

The second type of monomer, devoid of carboxylic function and which is ethylenically unsaturated, may be selected in a nonlimitative manner from the group comprising acrylic acid esters or methacrylic acid esters such as methyl, ethyl, butyl, 2-ethylhexyl, lauryl acrylates or methacrylates, acrylates and methacrylates of ethylene glycol, propylene glycol, polyethylene glycol and polypropylene glycol, as well as corresponding phosphates and sulfates; acrylonitrile, acrylamide, N-methylolacrylamide, dimethylaminoethyl acrylates and methacrylates, allyl alcohol, vinyl acetate, acrylamidomethyl-propanesulfonic acid, styrene and methylstyrene.

However, the second type of ethylenically unsaturated monomer is preferably selected from among acrylates, such as C<sub>1</sub>-C<sub>4</sub>-alkyl acrylates and methacrylates.

The third type of monomer, which is a surfactant monomer having at least one urethane function, results from the reaction of an ethylenically unsaturated isocyanate with a surfactant compound having a hydroxyl function that is reactive with regard to the -NCO group.

The ethylenically unsaturated isocyanate can be prepared by methods well known to persons skilled in the art, methods such as those described e. g. in U. S. Patent 2,718,516.

However, since these methods of preparation of ethylenically unsaturated isocyanates are relatively long, it is often preferable to use known ethylenically unsaturated monoisocyanates such as e. g. isocyanatoethyl methacrylate (sold by DOW CHEMICAL

COMPANY), or the meta or para isomers of  $\alpha$ ,  $\alpha$ -dimethylisopropylbenzyl isocyanate (sold by AMERICAN CYANAMID CORPORATION).

However, a preferred method of preparation consists in dropwise stoichiometric addition, to a diisocyanate, of an ethylenic compound having a single hydrogen that is active with regard to the –NCO groups under the reaction conditions chosen.

For the ethylenic compound it is possible to use, for example, acrylates and methacrylates of ethylene glycol, propylene glycol, polyethylene glycol and polypropylene glycol, allyl alcohol, allylamine, methallylamine and o-allylphenol.

For the diisocyanate, it is possible to use, for example, 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-trimethyl-1,6-diisocyanatohexane, 1,10-decamethylene diisocyanate, 4,4-methylene-bis-(isocyanatocyclohexane), 1,4-cyclohexylene diisocyanate, 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethylcyclohexane, m- and p-phenylene diisocyanate, 2,4- and 2,6-toluene diisocyanate, xylene diisocyanate, 4-chloro-1,3-phenylene diisocyanate, 4,4'-methylene diphenylisocyanate, 1,5-naphthalene diisocyanate, or tetrahydronaphthalene diisocyanate.

The surfactant compound having a hydroxyl function reactive with regard to the –NCO group of the ethylenically unsaturated isocyanate has the general formula:



wherein

- the term (O-R<sub>2</sub>) is ethylene oxide, propylene oxide, butylene oxide or a combination of at least two of these oxygen-containing groups;
- n, which represents the average number of terms present in said surfactant, has a value of between 5 and 150;
- the term R<sub>1</sub> is selected from the group consisting of hydrocarbon and/or amine chemical structures, such as aliphatic or cycloaliphatic alkyls, substituted or

unsubstituted aryls, polyaryls having 1 to 32 carbon atoms, secondary amines of formula  $(R_3)(R_4)N-$ , in which  $R_3$  and  $R_4$  are hydrocarbon groups having 1 to 20 carbon atoms.

Thus, the surfactant compound provided with a hydroxyl function that is reactive with regard to the  $-NCO$  group may preferably be selected from ethoxylated dilaurylamines, ethoxylated octyl and nonyl phenols, ethoxylated lauric, stearic, cetyl alcohols, ethoxylated mono-, di- and tristeryl phenols, taken alone or in a mixture.

Preferably, the term  $R_1$  is selected from among the  $C_{12}$  to  $C_{30}$  hydrocarbon chains, the term  $-O-R_2$  from the ethylene and/or propylene oxides, and  $n$  in the range of 15 to 50.

The associative thickening copolymer according to the invention contains, expressed in terms of percent by weight:

- a) from 15 to 75 % and preferably 30 to 45 % of other ethylenically unsaturated monomer(s) having at least one carboxyl function;
- b) from 25 to 70 %, preferably 45 to 60 % of other ethylenically unsaturated surfactant monomer(s) devoid of carboxyl function,
- c) from 0.5 to 35 %, preferably 4 to 15 % of surfactant monomer(s) having at least one urethane function resulting from the reaction of an ethylenically unsaturated isocyanate with a surfactant compound having at least one function that is reactive with regard to the  $-NCO$  group, the total of components (a), (b) and (c) being equal to 100.

The associative thickening copolymer according to the invention, i. e. that having a Brookfield viscosity at 100 rpm of at most equal to 220 centipoise under the above-mentioned conditions is prepared by known radical copolymerization processes, in solution, in emulsion or in suspension, of the mixture of the above-mentioned monomers, in the presence of a catalytic system and of known transfer agents used in appropriate amounts, the molecular weight of said copolymer being adjusted by the

following means: temperature, amount of catalyst, presence of a transfer agent or any other means or combination of means known to persons skilled in the art.

The catalytic system of polymerization is desirably selected from among those that are water-soluble, such as sodium persulfates, potassium persulfates, ammonium persulfates, used in combination with a known reducing compound such as sodium metabisulfite.

The amount of catalytic system of polymerization can vary between 0.1 % and 2 % by weight of the total weight of monomers used for obtaining the copolymer according to the invention.

The transfer agent is desirably selected from among the alkyl mercaptans such as octanethiol, decanethiol, n-dodecanethiol and tert.-dodecanethiol.

The amount of transfer agent can vary between 0 % and 5.0 % by weight relative to the total weight of the monomers present.

The copolymerization temperature can vary between 30 °C and 150 °C. It is preferably selected to be lower than the lowest boiling point of the components present under the experimental conditions.

The copolymers according to the invention develop their thickening property in an alkaline medium, in such a way that the carboxyl functions present are totally or partially neutralized, the neutralization agent preferably being lithium hydroxide, sodium hydroxide, potassium hydroxide, ammonium hydroxide, calcium hydroxide, magnesium hydroxide, an amine, or a combination of these agents.

The invention also relates to charged and/or pigmented aqueous compositions containing the copolymer according to the invention.

The charged and/or pigmented aqueous compositions are more particularly

those which, white or colored, contain, as principal constituents, an aqueous phase, charges and/or pigments, a natural or synthetic binder, and possibly, as secondary constituents, a dispersing agent, adjuvants as diverse as coalescence agents, biocides, surfactants, antifoaming agents or others, and the associative thickening copolymer according to the invention.

The associative thickening copolymer according to the invention is introduced into said compositions in an amount of 0.1 to 10 %, preferably 0.1 to 5.0 %, and quite preferably 0.4 to 1.5 %, calculated in percent by dry weight based on the total weight of the composition.

In practice, the liquid phase resulting from the copolymerization can be used in that form as associative thickening agent, but it can also be dried by any method known for eliminating this phase and isolate the copolymer in the form of a fine powder and used in this other form as associative thickening agent.

The associative thickening copolymer according to the invention is used in charged and/or pigmented aqueous compositions such as coating compositions, and more particularly paints, coating slips, printing pastes, leather finishing products, compositions for cosmetics and detergents, and drilling fluids.

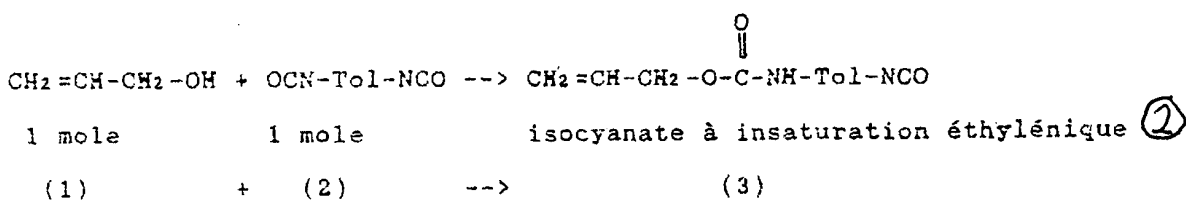
The scope and importance of the invention will be better understood by means of the following examples.

### Example 1

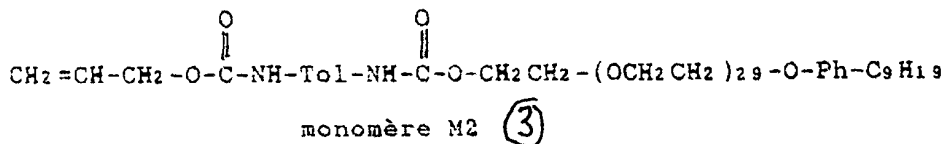
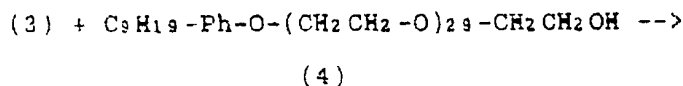
The object of this example is to illustrate the preparation of a surfactant monomer resulting from the reaction of an ethylenically unsaturated isocyanate with a surfactant compound having a hydroxyl function that is reactive with regard to the -NCO group.

To this end, the surfactant monomer was prepared in accordance with the following reaction scheme:

Etape 1 ①



Etape 2



Tol :  $\text{C}_6\text{H}_5-\text{CH}_3$

Ph :  $\text{C}_6\text{H}_4$

**Glossary:** 1 – Step 1; 2 - ethylenically unsaturated isocyanate; 3 - monomer M2

- (1) : Source of ethylenic unsaturation
- (2) : Diisocyanate
- (3) : Ethylenically unsaturated isocyanate
- (4) : Surfactant compound (alcohol)
- (5) : Ethylenically unsaturated surfactant monomer

wherein (3), the ethylenically unsaturated isocyanate, reacts with (4), which is the surfactant compound.

The preparation was carried out according to the following steps:

In a reactor equipped with a mechanical stirrer and a Dean-Stark separator surmounted by a reflux condenser were placed 154 grams of nonylphenol poly(ethyleneoxy)<sub>29</sub> ethanol and 200 grams of heptane. The mixture was then heated to 90 °C to dehydrate the surfactant. When the amount of water collected in the separator no longer changed, the heptane was distilled first at atmospheric pressure and then under reduced pressure (5 mm Hg). The mixture was then cooled, then maintained at the melting temperature of the surfactant.

17.4 grams of toluene diisocyanate, 3 drops of alloocimene (polymerization inhibitor) and 0.24 gram of dibutyltin dilaurate (catalyst) were placed in a beaker. The beaker was placed in a water-ice bath and magnetically stirred at 50 rpm.

5.8 grams of allyl alcohol kept on a molecular sieve is placed in a dropping funnel. The allyl alcohol was dropwise added in 30 minutes to the toluene diisocyanate, in such a way that the temperature of the reaction medium does not exceed 20 °C. The medium was then stirred until determination of the NCO groups indicates that 50 % of the isocyanate functions has reacted. The content of the beaker was then poured in the reactor containing the molten surfactant alcohol. The medium was then left under stirring for 2 hours. Determination of the NCO groups then showed that all the isocyanate functions initially present had disappeared. In this manner a surfactant monomer having two urethane bonds was quantitatively obtained. This product is the monomer M2 of Table I.

This synthesis procedure was repeated using other isocyanates having an ethylenic unsaturation, and other surfactant compounds (alcohols), by adjusting the quantities of

reagents so as to respect the stoichiometry of the reaction. In this way a series of surfactant monomers listed in Table I under references M1 to M88 were obtained.

However, in the case of monomers M51 to M70 which use commercially available ethylenically unsaturated isocyanates, Step 1 of the above-indicated scheme does not exist.

**TABLE I**

**Preparation of surfactant monomers**

① référence du monomère surfactant	② source d' insaturation éthylénique	diisocyanate	③ alcool surfactant	
			B	n
M1	④ alcool allylique	TDI	NP	50
M2	alcool allylique	TDI	NP	30
M3	alcool allylique	TDI	NP	17
M4	alcool allylique	TDI	C12	23
M5	alcool allylique	TDI	C12	17
M6	alcool allylique	TDI	C12	11
M7	alcool allylique	TDI	C16-18	25
M8	alcool allylique	TDI	C16-18	33
M9	alcool allylique	TDI	C16-18	50
M10	alcool allylique	TDI	⑤ Distyrylphénol	15
M11	MABG	TDI	NP	50
M12	MABG	TDI	NP	30
M13	MABG	TDI	NP	17
M14	MABG	TDI	C12	23
M15	MABG	TDI	C12	17
M16	MABG	TDI	C12	11
M17	MABG	TDI	C16-18	25
M18	MABG	TDI	C16-18	33
M19	MABG	TDI	C16-18	50
M20	MABG	TDI	Distyrylphénol	15
M21	MA (PEG)10	TDI	NP	50
M22	MA (PEG)10	TDI	NP	30
M23	MA (PEG)10	TDI	NP	17
M24	MA (PEG)10	TDI	C12	23
M25	MA (PEG)10	TDI	C12	17
M26	MA (PEG)10	TDI	C12	11
M27	MA (PEG)10	TDI	C16-18	25
M28	MA (PEG)10	TDI	C16-18	33
M29	MA (PEG)10	TDI	C16-18	50
M30	MA (PEG)10	TDI	Distyrylphénol	15

**Glossary:** 1- Reference, surfactant monomer; 2- Source of ethylenic unsaturation;  
3 – Surfactant alcohol; 4- Allyl alcohol; 5 – Distyrylphenol

**TABLE I (continued)**

① référence du monomère surfactant	② source d' insaturation éthylénique	diisocyanate	③ alcool surfactant	
			R	n
N31	④ Allylamine	TDI	NP	50
N32	Allylamine	TDI	NP	30
N33	Allylamine	TDI	NP	17
N34	Allylamine	TDI	C12	23
N35	Allylamine	TDI	C12	17
N36	Allylamine	TDI	C12	11
N37	Allylamine	TDI	C16-18	25
N38	Allylamine	TDI	C16-18	33
N39	Allylamine	TDI	C16-18	50
N40	Allylamine	TDI	⑤ Distyrylphénol	15
N41	ABG	TDI	NP	50
N42	ABG	TDI	NP	30
N43	ABG	TDI	NP	17
N44	ABG	TDI	C12	23
N45	ABG	TDI	C12	17
N46	ABG	TDI	C12	11
N47	ABG	TDI	C16-18	25
N48	ABG	TDI	C16-18	33
N49	ABG	TDI	C16-18	50
N50	ABG	TDI	Distyrylphénol	15
N51	α-TMI	/	NP	50
N52	α-TMI	/	NP	30
N53	α-TMI	/	NP	17
N54	α-TMI	/	C12	23
N55	α-TMI	/	C12	17
N56	α-TMI	/	C12	11
N57	α-TMI	/	C16-18	25
N58	α-TMI	/	C16-18	33
N59	α-TMI	/	C16-18	50
N60	α-TMI	/	Distyrylphénol	15

**Glossary:** 1- Reference, surfactant monomer; 2- Source of ethylenic unsaturation;  
3 – Surfactant alcohol; 4- Allylamine; 5 – Distyrylphenol

**TABLE I (continued)**

(1) référence du monomère surfactant	(2) source d' insaturation éthylénique	diisocyanate	(3) alcool surfactant	
			R	n
M61	IEH	/	NP	50
M62	IEH	/	NP	30
M63	IEH	/	NP	17
M64	IEH	/	C12	23
M65	IEH	/	C12	17
M66	IEH	/	C12	11
M67	IEH	/	C16-18	25
M68	IEH	/	C16-18	33
M69	IEH	/	C16-18	50
M70	IEH	/	(5) Distyrylphénol	15
M71	(4) alcool allylique	IPDI	NP	50
M72	alcool allylique	IPDI	NP	30
M73	alcool allylique	IPDI	NP	17
M74	alcool allylique	IPDI	C12	23
M75	alcool allylique	IPDI	C12	17
M76	alcool allylique	IPDI	C12	11
M77	alcool allylique	IPDI	C16-18	25
M78	alcool allylique	IPDI	C16-18	33
M79	alcool allylique	IPDI	C16-18	50
M80	alcool allylique	IPDI	Distyrylphénol	15
M81	MAGG	IPDI	NP	50
M82	ABG	IPDI	NP	50
M83	MA (PEG)10	IPDI	NP	50
M84	(6) allylamine	IPDI	NP	50
M85	MAGG	TDI	(C12)2-N	50
M86	ABG	TDI	(C12)2-N	50
M87	MA (PEG)10	TDI	(C12)2-N	50
M88	allylamine	TDI	(C12)2-N	50

**Glossary:** 1- Reference, surfactant monomer; 2- Source of ethylenic unsaturation;  
3 - Surfactant alcohol; 4- Allyl alcohol; 5 - Distyrylphenol; 6 - Allylamine

[Table I, explanation of abbreviations]:

MAEG	= ethylene glycol methacrylate
MA (PEG) 10	= poly(ethyleneoxy)9 ethanol methacrylate
TDI	= toluene diisocyanate
R	= hydrocarbon radical
n	= average number of ethylene oxide groups
NP	= nonylphenol radical
C12	= lauryl radical
C16-18	= ceto-stearyl radical
AEG	= ethylene glycol acrylate
m-TMI	= m-isopropenyl dimethylbenzyl isocyanate
IEM	= isocyanatoethyl methacrylate
IPDI	= isophorone diisocyanate
(C12)2-N	= dilaurylamine radical

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### Example 2

This example illustrates the preparation of an associative thickening copolymer according to the invention by using the surfactant monomer M2 of Table I.

To this end a pre-emulsion of monomers was first prepared by adding, in the indicated order and under stirring, the following compounds in the weight amounts shown:

Bipermuted water	155.00 g
Na lauryl ether sulfate (powder)	1.75 g
n-Dodecanethiol	0.95 g
Ethyl acrylate	147.50 g
Surfactant monomer M2	25.00 g
Methacrylic acid	100.00 g

In a reactor equipped with a reflux condenser and mechanical stirrer were placed, in the indicated weight amounts,

Bipermuted water	506.00 g
Na lauryl ether sulfate (powder)	2.35 g

The contents of the reactor were brought to 68 °C. 1 gram of ammonium persulfate dissolved in 5 grams of water, and 0.1 gram of sodium metabisulfite dissolved in 5 grams of water were then added. The pre-emulsion of monomers was then continuously introduced for 2 hours and the temperature in the reactor was maintained at 75 °C. The reaction medium was brought to 80 °C for 1 hour, then cooled. In this way an emulsion containing 28.7 % by weight of dry material of associative thickening copolymer W of Table II was obtained. A 2 % aqueous solution of said dry copolymer brought to pH 9 by the addition of ammonia had a viscosity of 120 cP (Brookfield RVT, mobile 2, 100 rpm, 20 °C).

This method of preparation was repeated by using different ethylenically unsaturated surfactant monomers such as those prepared according to Example 1. In this way a series of associative thickening copolymers according to the invention was obtained in the form of an emulsion (references A to AR in Table II).

In this table, and in accordance with the invention, the associative thickening copolymers placed into an aqueous solution containing 2 % dry matter and brought to a pH of 9 by the addition of ammonia and having a temperature of 20 ° all had a Brookfield (type RVT) viscosity at 100 rpm of at most equal to 220 centipoises.

**TABLE II**  
**Syntheses of copolymers according to the invention**

référence du copolymère ①	référence du monomère MS ②	% monomères ③			% nDDT	viscosité solution 2% à pH 9 100 tr/mn ④
		MS	AMA	ABt		
A	M1	9,2	36,7	54,1	0,37	90
B	M4	4,6	39,1	56,3	0,37	54
C	M24	9,2	36,7	54,1	0,26	55
D	M26	9,2	36,7	54,1	0,26	120
E	M4	9,2	36,7	54,1	0,57	63
F	M14	11,4	35,8	52,8	0,18	116
G	M4	11,4	35,8	52,8	0,47	100
H	M14	9,2	36,7	54,1	0,28	72
I	M6	9,4	37,8	52,8	0,87	47
J	M6	9,4	37,8	52,8	0,66	85
K	M5	9,2	36,7	54,1	0,61	82
L	M7	9,2	36,7	54,1	0,83	71
M	M8	9,2	36,7	54,1	0,60	41
N	M8	9,2	36,7	54,1	0,49	57
P	M6	9,2	36,7	54,1	0,66	87
Q	M8	9,2	36,7	54,1	0,39	90
R	M4	9,2	36,7	54,1	0,50	70
S	M8	9,2	36,7	54,1	0,50	58
T	M3	9,2	36,7	54,1	0,40	156
U	M9	9,2	36,7	54,1	0,40	132
V	M3	9,2	36,7	54,1	0,60	65
W	M2	9,2	36,7	54,1	0,35	120
X	M1	9,2	36,7	54,1	0,59	70
Y	M2	9,2	36,7	54,1	0,50	77
Z	M1	9,2	36,7	54,1	0,40	88
AA	M14	4,3	36,1	59,6	0,26	95
AD	M14	6,9	37,6	55,5	0,28	59
AC	M14	13,8	34,8	51,4	0,28	73
AD	M14	11,5	35,7	52,7	0,18	99
AE	M14	9,2	36,7	54,1	0,13	208
AF	M34	9,2	36,7	54,1	0,50	45
AG	M10	9,2	36,7	54,1	0,50	132
AH	M14	10,0	30,0	60,0	0,28	67
AI	M14	10,0	20,0	70,0	0,28	41
AJ	M14	10,0	40,0	50,0	0,28	82
AK	M14	15,0	55,0	30,0	0,28	87
AL	M14	10,0	45,0	45,0	0,28	78
AM	M14	15,0	15,0	70,0	0,28	30
AN	M14	14,3	23,8	61,9	0,28	37
AP	M14	20,0	30,0	50,0	0,28	91
AQ	M14	5,0	55,0	40,0	0,28	65
AR	M54	9,2	36,7	54,1	0,15	58

*Glossary:* 1 – Reference, copolymer; 2 – Reference, monomer MS; 3 - % monomers;  
4 – Viscosity of 2 % solution at pH 9 and 100 rpm.

AMA = methacrylic acid; Abt = ethyl acrylat ; MS = surfactant monomer, nDDT = n-dodecanethiol

### Example 3

The object of this example is to compare associative thickening copolymers, objects of the invention taken from Table II, to commercially available prior-art associative thickening agents.

Among the prior-art associative thickening agents, three of them, reputed to be among the best, were selected for this comparative study.

The first one, called alpha in the text which follows, is PRIMAL RM5, sold by ROHM & HAAS Co.

The second, called beta in the text which follows, is VISCALEX VG2, sold by ALLIED COLLOIDS Co.

The third, called gamma in the following text, is MOWILITH LDM 7000, sold by HOECHST Co.

To carry out this comparison, a series of white gloss aqueous paints was prepared in which only the nature and amount of the associative thickening agents changed.

These paints were formulated from an orientation formula proposed by producers of binding agents to formulators for the binding agent currently used in this type of paint.

The amounts of components of said paints, excluding the thickening agents that are the objects of the comparison, were expressed in grams, whereas the amount of thickening agent was expressed in % of dry polymer relative to the total of each formulation.

The formulations used were compiled in Table III-A and the results in Table III-B.

TABLE III-A

	Épaississant (1)					
	alpha	beta	gamma	H	H	U
référence peinture blanche (2)	3-1	3-2	3-3	3-4	3-5	3-6
Formule peinture blanche: (3)						
(4) coalescent : Propylène glycol						
(5) eau						
(6) dispersant : Coatex DR 3 (a)						
(7) bactéricide: Mergal K6N (b)						
(8) antimoine : Nopco MDW (c)						
(9) pigment : TiO2 RM02 (d)						
(10) liant : Primal HG 74 (e)						
(11) coalescent : méthoxybutanol						
(12) coalescent : Texanol (f)						
(13) ammoniac (28%)						
(14) épaisissant (% sec/total formule)	0,82	0,82	0,82	0,82	0,62	0,82
(15) antimoine : Nopco MDW						
(16) ammoniac (28%)						
(17) eau						
total						

Glossary: 1 – Thickening agent; 2 – Reference, white paint; 3 – Formula, white paint; 4 – Coalescent: Propylene glycol; 5 – water; 6 – dispersant; 7 – bactericide; 8 – antifoaming agent; 9 – binding agent; 10 – coalescent: methoxybutanol; 11 – ammonia; 12 – thickening agent (% dry / total formula); 13 – ammonia (28 %), qsp = q. s.

Commercialisé par la société = Sold by the ... Co. RFA = Federal Republic of Germany.

To use the results of Table III-B, it is desirable to define the methods and/or means employed for obtaining said results.

### **Viscosity 24 hours**

This viscosity was measured in a systematic manner 24 hours after producing each white paint.

The measurement was carried out by means of a Brookfield RVT viscosimeter at 20 °C using a mobile so chosen as to obtain a needle deviation within the graduation range of 15 to 80. The resulting value is representative of the viscosity of said paints in the can (viscosity under low shearing stress).

### **Apparent viscosity**

This measurement was carried out with the aid of a CONTRAVES type RHEOMAT 30 rheometer.

To this end, a small amount of paint was placed in the air gap (50  $\mu\text{m}$ ) of an HS 50 mobile, and the shearing stress ( $\tau$ ) as a function of the velocity gradient (D) was recorded. The apparent viscosity is the ratio  $\tau/D$  for  $D = 17700 \text{ sec}^{-1}$ .

The shearing stress at  $17700 \text{ sec}^{-1}$  is representative of the high shearing stresses met with during the use of paints applied by brush or roller. Hence the measured apparent viscosity seems to be a means of observing the potential behavior of the paint when using a brush or roller.

## **Yield value**

This measurement was also carried out with the aid of a CONTRAVES type RHEOMAT 30 rheometer, using a DIN 25 mobile.

To carry out this yield-value measurement, the paint was first subjected to high shearing stress (about  $500 \text{ sec}^{-1}$ ) in order to destructure it. Then the shearing stress as a function of velocity-gradient (D) curve was recorded, said gradient varying from 0 to  $5 \text{ sec}^{-1}$ . The intersection of the tangent at the low point of the curve and the shearing-stress axis gives the yield value.

## **Film tension**

The film tension after application defines the ability of the paints to level out the thickness irregularities caused by their application on a substrate to be protected. To measure it, a simulation of the irregularities was carried out by depositing on a glass plate five pairs of cords having an initial rectangular cross section, the deposits of each pair being separated by a 2 millimeter interval. The thicknesses of the cords are 0.25 mm, 0.50 mm, 1 mm, 2 mm and 4 mm. The plate was maintained in a horizontal position. After drying, the number of deposit pairs whose cords became joined was noted. Hence the best film tension is 5, i. e. all cord pairs are joined, and the worst was 0, i. e. no pair became joined.

## **Resistance to running**

The resistance to running defines the ability of a paint to resist flowing off after its application to a substrate to be protected.

To measure it, 10 cords 6 mm wide and between 75 and 300 microns thick were deposited on a glass plate by means of a gauge, in increments of 25 microns, the different deposits being separated by an interval of 2 millimeters. The plate is then placed vertically, the thickest deposits being placed at the bottom. After drying, the number of unjoined bands were noted. Hence the best resistance to running is 10 and the worst 0.

The last two measurements, namely film tension and resistance to running, were carried out according to the standard ASTM D 2801-69.

### **Gloss**

Measurement of the gloss, whose technique is well known to persons skilled in the art, was carried out by using an ERICHSEN gloss meter on dry film after 24 hours.

### **Application**

After applying the paint with a brush to a kraft-type substrate, the operator, using his know-how, judged three qualities of application, namely brushability, film tension and covering power, using the following notations:

- Brushability      A = excellent  
                            B = good  
                            C = average  
                            D = difficult to apply  
                            E = very difficult to apply,

the brushability reflecting the more or less agreeable sensation that the user feels during application of the film.

- Film tension
  - A = excellent
  - B = good
  - C = stretches fairly well
  - D = cords a little
  - E = cords a lot
  
- Covering power
  - A = covers very well
  - B = covers well
  - C = covers fairly well
  - D = covers little
  - E = covers poorly

All the results relating to the above-mentioned tests have been assembled in Table III-B.

TABLE III-B

Epaississant (% sec / total formule) (1)							
	alpha 0,82	beta 0,82	gamma 0,82	H 0,82	H 0,62	E 0,82	G 0,82
(2) référence peinture blanche	3-1	3-2	3-3	3-4	3-5	3-6	3-7
pH	8,7	8,7	8,8	8,7	8,7	8,7	8,7
(3) viscosité	2800	11800	11600	7200	6000	4500	6800
{ Brookfield :							
(4) 24 heures (cP)	1600	2650	3300	3880	3440	2780	3840
(5) viscosité apparente (mPa.s)	186	130	191	331	222	209	241
(6) Limite d'écoulement (Pa)	1,30	12,50	11,00	3,20	2,20	1,30	2,10
(7) tension du film	3	2	2	2	3	3	3
(8) résistance à la coulure	2	9	9	9	7	8	9
(9) brillance (%)	68	67	71	67	68	65	67
(10) 24 heures	85	85	87	86	85	84	86
	95	94	96	95	95	94	94
(11) application:	D	D	C	C	B	A	B
(12) { brossabilité	C	E	D	B	B	B	B
{ tension du film	C	E	D	B	B	B	B
{ pouvoir	C	E	C	A	A	B	A
{ gommant							

Glossary: 1 – Thickening agent (% dry / total formula); 2 – reference, white paint; 3 – Brookfield viscosity 10 rpm; 4 – 24 hours (cP) 100 rpm; 5 – apparent viscosity (mPa.s); 6 - Yield value (Pa); 7 – film tension; 8 – resistance to running; 9 – gloss (%); 10 – 24 hours; 11 – application: brushability; 12 – covering power

From Table III-B it can be noted that the apparent viscosity of the paints thickened by means of the associative copolymers according to the invention is always greater than 200 mPa.s, whereas the apparent viscosity of the paints thickened with the aid of currently sold thickening agents and part of the prior art is always below 200 mPa.s, at constant amounts of thickening agent,

In the case of paint 3-4 (object of the invention) the apparent viscosity is 70 % higher than the best apparent viscosity of prior-art paints.

In the case of paints 3-1 to 3-3, which are prior-art paints, It has been noted that

- for paint 3-1, the viscosity at 24 hours is too low and results in a mediocre resistance to running;
- for paints 3-2 and 3-3 this viscosity at 24 hours is too high and results in a yield value that is too high, which is reflected , on application of the paint, by a bad film tension (cording effect).

For paints 3-4 and 3-5, objects of the invention, decrease of the amount of thickening agent (24 % decrease with respect to the prior art) makes it possible to keep the apparent viscosity at a favorable level, always greater than 200 mPa.s while decreasing the viscosity at 24 hours and the yield value, making it possible without any impairment of the covering power, to improve the film tension and the brushability.

As for paints 3-6 and 3-7 which are also objects of the invention, they offer rheological characteristics and applications that are better than the prior-art characteristics.

#### Example 4

The object of this example is to compare the associative thickening copolymers, objects of the invention from Table II, to commercially available prior-art associative thickening agents.

Used as prior-art associative thickening agents were the three agents alpha, beta and gamma defined in Example 3.

These paints were formulated from an orientation formula proposed by the manufacturer of binding agents to the formulators for the binding agent used and currently employed in this type of paint.

The amounts of the components of said paints, excluding the thickening agents that are objects of the comparison, were expressed in grams, whereas the amount of thickening agent was expressed as a percentage of dry polymer calculated on the total of each formulation.

The formulations used are listed in Table IV-A and the results in Table IV-B.

The tests listed in Table IV-B were carried out in accordance with the definitions given in Example 3.

All results relating to the aforementioned tests were assembled in Table IV-B.

TABLE IV-A

référence peinture blanche (2)	épaississant (1)				
	gamma	beta	alpha	H	H
	4-1	4-2	4-3	4-4	4-5
(3) Formule peinture blanche:					
(4) eau	25,00				
dispersant : Coatex DB3 (a)	4,00				
(5) antimoine : Tego Ronaex 1408 (b)	0,80				
(6) bactéricide: Kergal K6H (c)	2,20				
(7) coalescent : propylène glycol	25,00				
pigment : TiO2 RMD2 (d)	210,00				
(8) liant : Novilith LDK 7770 (e)	600,00				
(7) coalescent : propylène glycol	75,00				
coalescent : Texanol (f)	15,00				
(9) ammoniacque (28%)	4,40				
(10) épaississant (Ksec/total formule)	0,58	0,58	0,58	0,58	0,43
(4) eau	qsp total 1024				
(9) ammoniacque (28%)	qsp pH 8,7				
total	1024,00				

Glossary: 1 – Thickening agent; 2 – Reference, white paint; 3 – Formula, white paint; 4 – water; 5 – antifoaming agent; 6 – bactericide; 7 – coalescent: propylene glycol; 8 – binding agent; 9 - ammonia; 10 – thickening agent (% dry / total formula); qsp = q. s.

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TABLE IV-B

Epaississant (% sec / total formula) (1)					
	gamma	beta	alpha	H	H
	0,58	0,58	0,58	0,58	0,43
référence peinture blanche (2)	4-1	4-2	4-3	4-4	4-5
pH	8,7	8,7	8,7	8,7	8,7
(3) viscosité Brookfield : 10 tr/mn	4800	1600	2600	6000	3400
(5) 24 heures (cP)	1440	740	1280	2840	1800
(5) viscosité apparente (mPa.s)	149	86	122	214	161
(6) limite d'écoulement (Pa)	1,00	0,50	0,10	2,30	0,80
(7) tension du film	3	5	5	4	4
(9) résistance à la coulure	5	0	1	7	7
(9) brillance (%)	59	60	64	64	61
(4) 24 heures	73	75	79	81	80
	75	78	81	84	87
application:	D	E	E	A	B
(10) brossabilité	C	B	A	A	A
(7) tension du film	C	E	D	A	B
(11) pouvoir garnissant	C	E	D	A	B

**Glossary:** 1 – Thickening agent (% dry / total formula); 2 – reference, white paint; 3 – Brookfield viscosity 10 rpm; 4 – 24 hours (cP) 100 rpm; 5 – apparent viscosity (mPa.s); 6 - Yield value (Pa); 7 – film tension; 8 – resistance to running; 9 – gloss (%); 10 – brushability; 11 – covering power

Table IV-B, in combination with Table III-B, shows the evident superiority of the associative thickening agent H according to the invention. In effect, at identical concentrations of thickening agent, the apparent viscosity of paint 4-4 (object of the invention) is 40 % higher than the best apparent viscosity of the prior-art paintings (4-1 to 4-3).

In the case of paints 4-4 and 4-5 which are the object of the invention, the 26 % decrease in the amount of thickening agent (paint 4-5) leads to a paint whose rheological and use characteristics are always superior to those of the prior-art paints (4-1 to 4-3).

#### Example 5

The object of this example is to compare the associative thickening copolymers, objects of the invention from Table II, to commercially available associative thickening agents of the prior art.

Used as prior-art associative thickening agents were the three agents alpha, beta and gamma, defined in Example 3.

These paints were formulated from an orientation formula proposed by the manufacturer of binding agents to the formulators for the binding agent used and currently employed in this type of paint.

The amounts of the components of said paints, excluding the thickening agents that are objects of the comparison, were expressed in grams, whereas the amount of thickening agent was expressed as a percentage of dry polymer calculated on the total for each formulation.

The formulations used are listed in Table V-A and the results in Table V-B.

TABLE V-A

référence peinture blanche (2)	épaississant (1)					
	alpha	beta	beta	gamma	gamma	H
	5-1	5-2	5-3	5-4	5-5	5-6
(3) Paraulle peinture blanche:						
(4) coalescent : propylène glycol	24,30					
(5) eau	31,80					
dispersant : Coatex DM3 (a)	4,00					
(6) bactéricide: Kergal KGN (b)	1,50					
(7) antiaousse : Dyl 073 (c)	1,00					
pigment : TiO2 RHD2 (d)	230,30					
(8) ammoniacque (28%)	2,50					
(9) coalescent : éthyl diglycol	24,50					
(10) coalescent : butyl diglycol	24,50					
(11) liant : Néocryl XK 76 (e)	580,60					
(12) épaississant (% sec /total formule)	1,10	0,50	1,10	0,40	1,10	1,10
(5) eau	qsp total 1000					
(7) antiaousse : Dyl 073	1,00					
(8) ammoniacque (28%)	qsp pH 8,7					
total	1000,00					

Glossary: 1 – Thickening agent; 2 – Reference, white paint; 3 – Formula, white paint; 4 – coalescent: propylene glycol; 5 - water; 6 – bactericide; 7 – antifoaming agent; 8 – ammonia; 9 – coalescent: ethyl diglycol; 10 – coalescent: butyl diglycol; 11 – binding agent; 12 – thickening agent (% dry / total formula); qsp = q.s.

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**TABLE V-B**

Epaississant (% sec / total formule) (1)						
	alpha 1,10	beta 0,50	beta 1,10	gamma 0,40	gamma 1,10	H 1,10
référence peinture blanche (2)	5-1	5-2	5-3	5-4	5-5	5-6
pH	8,7	8,7	8,7	8,7	8,7	8,7
(3) viscosité 10 tr/mm	5000	4000	9500	3400	13300	3600
(4) Brookfield :						
(5) 24 heures (cP)	1720	1040	2570	760	2960	2320
(6) viscosité apparente (mPa.s)	172	65	153	61	186	245
(7) limite d'écoulement (Pa)	2,00	6,00	6,30	4,20	11,20	1,50
(8) tension du film	3	1	3	3	0	3
(9) résistance à la coulure	7	8	9	7	9	6
(10) brillance	54	53	56	52	57	54
(11) 24 heures	76	75	78	73	77	76
	84	87	88	84	89	88
	85°					
application:						
(10) brossabilité	C	D	C	D	C	A
(11) tension du film	C	D	E	C	E	A
(11) pouvoir garrissant	A	E	B	E	B	A

**Glossary:** 1 – Thickening agent (% dry material / total formula); 2 – reference, white paint; 3 – Brookfield viscosity 10 rpm; 4 – 24 hours (cP) 100 rpm; 5 – apparent viscosity (mPa.s); 6 - Yield value (Pa); 7 – film tension; 8 – resistance to running; 9 – gloss (%); 10 – brushability; 11 – covering power

The tests listed in Table V-B were carried out in accordance with the definitions given in Example 3.

All results relating to the aforementioned tests were assembled in Table V-B.

Table V-B, in conformity with Tables III-B and IV-B, shows that the paint formulated with the associative thickening agent according to the invention (5-6) in an amount of 1,1 % relative to the total weight of the formula has an apparent viscosity that is 30 % better than the prior-art paints (5-1, 5-3 and 5-5) for a same amount of dry thickening agent.

Moreover, in the case of the prior-art paints 5-3 and 5-5 the viscosities at 24 hours (in the can) are too high, producing yield values that are too great and which affect the film tension.

With a view to overcoming this phenomenon, decreasing the amount of thickening agent (references 5-2 and 5-4) produces a reasonable decrease of the viscosity at 24 hours, but a considerable decrease of the apparent viscosity, resulting in an unacceptable reduction of the covering power.

Hence, it appears from Examples 3, 4 and 5 that the acrylic associative thickening agents according to the invention impart to the paints in which they are used rheological and application characteristics which are always better than those of paints thickened by means of commercially available thickening agents reputed to be among the best.

These agents provide the paints not only with a high covering power (high apparent viscosity) but also with an excellent compromise between film tension and resistance to running, which characteristics are naturally antagonistic to one other. Moreover, these agents may be used in lower amounts than the prior art thickening agents, while retaining for the paints containing them better rheological and application characteristics than those of the paints formulated with prior-art thickening agents.

Finally, the thickening agents according to the invention show by the examples that they provide the paints containing them with a regularity of rheological and application characteristics that are not found in the paints formulated with prior-art thickening agents.

#### Example 6

The object of this example is to illustrate the influence of molecular weight of the associative thickening agent on its ability to be used in a formulation in a gloss aqueous painting.

More particularly, the object of this example is to prove that the molecular weight of said thickening agent must be less than a limit value in order that it retain an ability to be used in said paints, said limit value expressed in Brookfield viscosity being at most equal to 220 centipoises for a 2 % aqueous solution of the dry thickening agents brought to pH 9 by the addition of ammonia at a temperature of 20 °C and for a speed of 100 rpm and a mobile permitting an index deviation of between 15 and 80 at the time of measurement.

In this example, measurement of the RVT Brookfield viscosity relative to the molecular weight of each associative thickening agent tested is carried out not only at a concentration of 2 % but also at a concentration of 1 % of the dry thickening agent, according to the method of measurement described in U. S. Patent 4,514,552, so as to have a common means of measurement making it possible to compare the thickening agents according to the invention and the prior-art thickening agents described in said patent.

To this end, paints were prepared in quantitative and qualitative conformity with test 3-5 of Example 3, i. e. with the same binding agent, which is PRIMAL HG 74 from ROHM & HAAS.

Paints 6-1 and 6-3 contained prior-art thickening agents, and paints 6-5 and 6-6 contained thickening agents according to the invention, said thickening agents having been used in an amount of 0.62 % of dry product relative to the total of the formula.

Paints 6-2 and 6-4 contained prior-art thickening agents, but in lower amounts.

The results relating to the aforementioned paints and to the tests carried out on said paints, as they have been defined in Example 3, are assembled in Table VI.

TABLE VI

Selection of molecular weights adapted to the formulation of paints on the formula of Example 3

① {	référence peinture blanche	6-1	6-2	6-3	6-4	6-5	6-6	
②	référence du polymère	③ { art	art	art	art	AE	H	
④	nature du monomère	⑤ { antérieur alc allyl. TDI	antérieur alc allyl. TDI	antérieur MAEG TDI	antérieur MAEG TDI	MAEG MAEG TDI	MAEG MAEG TDI	
⑥	viscosité 2% (cP)	10 tr/mn 100 tr/mn	4800 1380	4800 1380	750 500	750 500	200 208	40 72
	viscosité 1% (cP)	10 tr/mn 100 tr/mn	800 244	800 244	220 172	220 172	40 70	20 52
⑦ {	% sec d'épaississant/total	0,62	0,25	0,62	0,17	0,62	0,62	
	pH	8,6	8,6	8,6	8,7	8,6	8,7	
⑧	viscosité Brookfield							
⑨	24 heures (cP)	10 tr/mn 100 tr/mn	27600 5250	3000 950	13400 5100	2500 830	7000 3100	6000 3440
⑩	viscosité apparente (mPa.s)		154	64	240	58	200	222
⑪	limite d'écoulement (Pa)		29,00	2,80	7,90	2,50	2,50	2,20
⑫	tension du film		0	3	2	3	3	3
⑬	résistance à la coulure		9	9	9	7	8	7
⑭	brillance (%)	20°	64	60	63	59	65	68
	24 heures	60°	85	82	81	80	83	85
		85°	89	89	88	87	91	95
	application:	⑮ brossabi- lité	C	C	C	C	A	B
		⑫ tension du film	E	B	D	C	B	B
		⑯ pouvoir garnissant	C	E	A	E	A	A

alc allyl. = alcool allylique

MAEG = méthacrylate d'éthylène glycol

TDI = toluène diisocyanate

C12 23 OE = lauryl poly(éthylèneoxy)22-éthanol

Glossary: 1 - reference, white paint; 2 - reference of .... polymer; 3 - prior art; 4 - nature of polymer; 5 - allyl alcohol; 6 - viscosity, 2 %; 10 rpm; 7 - % dry thickening agent / total; 8 - Brookfield viscosity; 9 - 24 hours; 10 - apparent viscosity; 11 - yield value (Pa); 12 - film tension; 13 - resistance to running; 15 - gloss; 15 - brushability; 16 - covering power.

MAEG = ethylene glycol methacrylate; TDI = toluene isocyanate; C12 23 OE = lauryl poly(ethyleneoxy)<sub>22</sub> ethanol

From this table the following observations can be made:

Paints 6-1 and 6-3 (relating to the prior art) have very high viscosities at 24 hours, which produce unacceptable yield values that are reflected by a very poor film tension (highly marked cording), even though the apparent viscosity of said paints is not affected by the thickening agents used.

The formulations of paints 6-5 and 6-6 (relating to the invention), which have apparent viscosities close to those measured in the case of the prior art, differ from the prior art by much lower 24-hour viscosities and yield values, which greatly favor the film tension, an essential criterion for the application of said paints.

The formulations of 6-2 (to be compared to 6-1) and 6-4 (to be compared to 6-3) which relate to the prior art, were the object of a decrease of the amount of thickening agent with a view to reducing the 24-hour viscosities and the excessive yield values in order to improve the film tension. However, from the results it appears that the decrease of the amount of thickening agent causes a redhibitory drop of the apparent viscosity and hence of the covering power.

Finally, as can be seen from U. S. Patent 4,514,552, the thickening agents described therein have a viscosity, in aqueous solution at a concentration of 1 % at 10 rpm, that is greater than or equal to 178 centipoises, while the viscosity of solutions of the copolymers according to the invention under the same conditions is at the most 40 centipoises, as indicated in Table VI.

Hence it is confirmed that the average molecular weights of the thickening agents must not exceed a limit value which is represented by the viscosity measured according to the aforementioned conditions at an amount of 2% of said agent, which is 220 centipoises at 100 rpm, in order that the thickening agents, which are objects of the invention, simultaneously impart to the paints in which they are used a good rheological

compromise at high and low shearing stresses, reflected simultaneously by a good covering power and excellent film tension, criteria which are never achieved by the paints formulated by using the type of thickening agents belonging to the prior art.

#### Example 7

The object of this example is to confirm the influence of the molecular weight of the thickening agent on its ability to be used in gloss aqueous paints based no longer on PRIMAL HG 74 as in Example 6, but on NEOCRYL XK 76 sold by POLYVINYL CHEMIE.

The paints tested were prepared in quantitative and qualitative conformity with test 5-1 of Example 5. except for the type of thickening agent and the amount in which it was used in said paints.

Paints 7-1 and 7-3 (of the prior art) and 7-5 and 7-6 (objects of the invention) used different thickening agents but in the same amount.

Paints 7-2 and 7-4 (of the prior art) used different thickening agents in lower amounts than for the other paints.

The results relating to the aforementioned paints and to the tests carried out on said paints as they have been defined in Example 3 are assembled in Table VII.

TABLE VII

Selection of the molecular weights adapted to the formulation of paints on the formula of Example 5

① référence peinture blanche:		7-1	7-2	7-3	7-4	7-5	7-6
② référence du polymère	art	antérieur alc allyl. ⑤	art antérieur alc allyl. ⑤	art antérieur MAEG	art antérieur MAEG	AE MAEG	M MAEG
④ nature du monomère	TDI	C12-23 OE	TDI C12-23 OE	TDI C12-23 OE	TDI C12-23 OE	TDI C12-23 OE	TDI C12-23 OE
viscosité 20%	10 tr/mn	4800	4800	750	750	200	40
(cP)	100 tr/mn	1380	1380	500	500	208	72
viscosité 10%	10 tr/mn	800	800	220	220	40	20
(cP)	100 tr/mn	244	244	172	172	70	52
⑦ 0% sec d'épaississant/total	pH	1,10	0,39	1,10	0,32	1,10	1,10
⑧ viscosité Brookfield	8,6	8,6	8,6	8,6	8,7	8,6	8,7
⑨ 24 heures	10 tr/mn	59000	4500	16500	4200	4500	3600
(cP)	100 tr/mn	13200	1200	6650	1050	2860	2320
⑩ viscosité apparente (mPa.s)		275	69	361	71	271	245
⑪ limite d'écoulement (Pa)		non mesurable	2,50	11,70	3,40	2,50	1,50
⑫ tension du film		0	3	1	3	3	3
⑬ résistance à la coulure		9	9	9	7	8	6
⑭ brillance (%)		55	51	54	50	53	54
⑮ 24 heures		72	71	74	72	75	76
		84	82	87	85	89	88
application:							
⑬ brossabilité	E	D	C	D	A	A	A
⑭ tension du film	E	B	D	C	B	A	A
⑮ pouvoir garnissant	A	E	B	E	A	A	A

Glossary: 1 - reference, white paint; 2 - reference of ... polymer; 3 - prior art; 4 - nature of polymer; 5 - allyl alcohol; 6 - viscosity, 2 %; 10 rpm; 7 - % dry / total; 8 - Brookfield viscosity; 9 - 24 hours; 10 - apparent viscosity; 11 - yield value (Pa); 12 - film tension; 13 - resistance to running; 14 - gloss; 15 - brushability; 16 - covering power.

MAEG = ethylene glycol methacrylate; TDI = toluene isocyanate; C12 23 OE = lauryl poly(ethyleneoxy)<sub>22</sub> ethanol

This table leads to the following conclusions. In the same way as in Example 6, the thickening agents used in paints 7-1 and 7-3 impart to them a very high viscosity at 24 hours and very high yield value, reflected by a very poor film tension (highly marked cording), even though the apparent viscosity of said formulations is not affected by the thickening agents used.

These same thickening agents used in smaller amounts (7-2 and 7-4) lead to acceptable viscosities at 24 hours and acceptable yield values, improving the film tension but destroying the apparent viscosity and hence the covering power at the application level.

The thickening agents objects of the invention responding to the selective limit of molecular weights according to the invention, impart to the paint formulation in which they are used an excellent rheological compromise at high and low shearing stresses, reflected simultaneously by a good covering power and good film tension, as has already been noted in Example 6.

#### Example 8

The object of this example is to show the superiority of the associative thickening agents according to the invention over the prior-art thickening agents from the point of view of their compatibility with colored inorganic or organic pigments present in the form of a pigment paste.

By compatibility with pigments, the sum total of the following observed effects is meant:

- absence of a substantial increase in the viscosity of the paint after addition of the pigment paste;
- absence of deterioration of the film tension of the colored paint,
- absence of pigment flotation, reflected by their rising to the surface of the paint can.

Understood by "pigment paste" is any concentrated suspension of inorganic or organic pigments introduced into a white paint in order to color it.

The pigment pastes used are described in Table VIII-A, and are currently used in the paint profession.

Thus, the white paints having at least one of the following disadvantages:

- too high viscosity in the can (i. e. Brookfield 24-hour viscosity) and too high yield value (resulting in a poor film tension: cases of tests 3-2, 5-3, 6-1, 6-3, 7-1 and 7-3).
- too low apparent viscosity (little covering power: case of tests 3-2, 4-2, 4-3, 5-2, 5-4, 6-2, 6-4, 7-2 and 7-4).

have been eliminated from the coloring tests.

By contrast, white paints showing a good rheological compromise at high and low shearing stresses (reflected by a good covering power and good film tension) were subjected to the coloring tests.

To this end, paints meeting the aforementioned selection criteria, chosen from Examples 3 to 5, were colored by the addition, under mechanical stirring, of 5 parts by weight of pigment paste per 100 parts by weight of white paint, this quantity having been chosen arbitrarily.

TABLE VIII-A  
References of pigment pastes

Pigment paste No.	Type	Commercial reference	Producer
1	Yellow iron oxide	Telochrome TC 21 EJ 603	Telosud
2	Red iron oxide	Telochrome TC 21 ER 317	Telosud
3	Chromium yellow	Telochrome TC 21 EJ 655	Telosud
4	Phthalocyanine blue	Luconyl 6900	BASF
5	Phthalocyanine green	Green 8J	Astra
6	Dinitraniline red	Red 2 J	Astra
7	Carbon black	Black V	Astra
8	Hansa yellow	Yellow 10J	Astra

The Brookfield viscosity at 24 hours of the colored paints was systematically measured in the can in order to note any appreciable increase in viscosity which would be injurious to the quality of the paint and which would be reflected by incompatibility between the thickening agent used and the pigment paste.

All results relating to this study are assembled in Table VIII-B and relate to the Brookfield 24-hour viscosity, to the possible floating of the pigments and to the quality of the color developed.

TABLE VIII-B

## Compatibility of thickening agents with pigment pastes

①	Liant	Neocryl XK76	Neocryl XK76	Primal HG74	Primal HG74	Mowilith LDM7770	Mowilith LDM7770	Mowilith LDM7770
		H	alpha	H	alpha	H	alpha	gamma
② {	Epaissis-							
③ {	sant							
④ {	Dose (a)	1,10	1,10	0,82	0,82	0,58	0,58	0,58
	Réfé-	5-6	5-1	3-4	3-1	4-4	4-3	4-1
	rence							
	peinture							
	blanche							
⑤ viscosité Brookfield (cP) 10 tr/mn								
⑥ 24 heures 100 tr/mn								
⑦ {	peinture	3600	5000	7200	2800	6000	2600	4800
	blanche	2320	1720	3800	1440	2840	1280	1440
⑧	Pâte N°:							
	1	4000	5600 ‡	7600	2800	6800 ‡	2800 ‡	4400
		2320	2080 \$	4300	1600	3440 \$	1520	1480
	2	3000	5200 ‡	6800	2800	6400 ‡	2600 ‡	4400
		1960	1960	3600 \$	1400	2880	1320	1400
	3	3600	9200	5600	3400	5600	3600	6000
		1960	2600	3080 \$	1560	2600	1680	1720
	4	5600	13200 ‡	7200	10400 ‡	4800	4800	7200
		2640	3280	3720	2320	1840	1840	2360
	5	4000	12400	6000	6000 ‡	4000	3400	7200
		1920	2720	2880	1960	2080	1520	1960
	6	3200	10400	3600	10000	3200	4800	6400
		1760	2720	2200	2080	1480 \$	1440	1680
	7	16000	20400	11400	15600	5200	6000	10800
		3400	3640	3880 \$	2920	2360 \$	2040	2600
	8	4000	11200	8400	4800	8000	4800	6800
		2400 \$	3000	4700 \$	1840	3560 \$	1840	2160
⑨ {	augmen-	2000	8200	1200	7600	2000	3400	2400
	tation							
	maximale							
	visco 10 tr							
⑩ {	moyenne	+ 250	+ 4600	-1000	+ 2400	-600	+ 1200	+ 1200
	variation							
	visco 10 tr							

Glossary: 1 - Binder; 2 - Thickening agent; 3 - Amount (a); 4 - Reference, white paint; 5 - Brookfield viscosity (cP) 10 rpm; 6 - at 24 hours 100 rpm; 7 - white paint; 8 - Paste No.; 9 - maximum increase in viscosity, 10 rpm; 10 - average variation of viscosity, 10 rpm

(a) % dry / total formula

‡ pigment flotation

\$ excellent color development

From this table, the following noticeable observations can be made:

- In the case of paints colored by means of pigment paste No. 7, the results are mediocre, except in one case (white paint 4-4, colored with pigment paste No. 7);
- With the exception of the paints formulated by means of pigment paste No. 7, the colored paints thickened by means of the thickening agent according to the invention show
  - very few cases of pigment flotation,
  - a color development that is at least always equivalent and often better than that obtained with the paints containing prior-art thickening agents, at identical binders and pigment pastes,
  - finally and especially a remarkable absence of redhibitory increase of the Brookfield 24-hour viscosity.

To illustrate the remarkable absence of redhibitory increase of this viscosity, Table VIII-B shows in the last two lines

- the maximum increase of Brookfield viscosity at 10 rpm in relation to the white paint,
- the average algebraic value of the variation of said viscosity.

The calculations were made by excluding the results obtained with pigment paste No. 7 which were found to be generally very mediocre whichever thickening agent was used, as has already been stated.

Thus, the maximum increases and the average values of the variation of viscosity show that only the colored paints containing the thickening agents of the invention are not subject to a redhibitory viscosity increase relative to the original white paint.

## Claims

1. Associative thickening copolymer water-soluble in a neutral or alkaline medium, for charged and/or pigmented, white or colored aqueous compositions, composed

a) of at least one ethylenically unsaturated monomer having at least one carboxylic function,

b) of at least one other ethylenically unsaturated monomer devoid of carboxylic function.

c) of at least one surfactant monomer having at least one urethane function resulting from the reaction of an ethylenically unsaturated isocyanate with a surfactant compound, having a hydroxyl function that is reactive towards the –NCO group,

characterized in that said copolymer belongs to the group consisting of those which, by definition, when placed in an aqueous solution containing 2 % by weight of dry matter and brought to pH 9 by the addition of ammonia, at a temperature of 20 °C, have a Brookfield viscosity at 100 rpm of at most equal to 220 centipoises.

2. Copolymer according to Claim 1, characterized in that the ethylenic monomer (a) having at least one carboxyl function is selected from the group comprising the monoacids acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, the diacids itaconic acid, fumaric acid, maleic acid, citraconic acid, maleic anhydride and the C<sub>1</sub> to C<sub>4</sub> half esters of diacids.

3. Copolymer according to Claims 1 or 2, characterized in that the carboxylated ethylenic monomer is preferably acrylic acid, methacrylic acid or itaconic acid.

4. Copolymer according to any one of Claims 1 to 3, characterized in that the ethylenically unsaturated monomer (b) devoid of carboxyl function is selected from the group comprising methyl, ethyl, butyl, 2-ethylhexyl, lauryl acrylates or methacrylates, ethylene glycol, propylene glycol, polyethylene glycol and polypropylene glycol acrylates and methacrylates and the corresponding phosphates and sulfates,

acrylonitrile, acrylamide, N-methylolacrylamide, dimethylaminoethyl acrylates and methacrylates, allyl alcohol, vinyl acetate, acrylamidomethyl-propanesulfonic acid, styrene and methylstyrene.

5. Copolymer according to any one of Claims 1 to 4, characterized in that the ethylenically unsaturated monomer (b) is preferably selected from among the C<sub>1</sub> to C<sub>4</sub> acrylates and methacrylates.

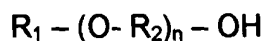
6. Copolymer according to any one of Claims 1 to 5, characterized in that the ethylenically unsaturated isocyanate involved in the make-up of the surfactant monomer (c) results from the reaction of a diisocyanate with an ethylenic compound having a function that is reactive towards the –NCO group.

7. Copolymer according to Claim 6, characterized in that the diisocyanate is selected from the group comprising 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-trimethyl-1,6-diisocyanatohexane, 1,10-decamethylene diisocyanate, 4,4-methylene-bis(isocyanatocyclohexane), 1,4-cyclohexylene diisocyanate, 1-isocyanato 3-isocyanatomethyl-3,5,5-trimethylcyclohexane, m- and p-phenylene diisocyanate, 2,4- and 2,6-toluene diisocyanate, xylene diisocyanate, 4-chloro-1,3-phenylene diisocyanate, 4,4'-methylene diphenylisocyanate, 1.5-naphthalene diisocyanate and tetrahydronaphthylene diisocyanate.

8. Copolymer according to Claim 6, characterized in that the ethylenic compound having a function reactive towards the –NCO group is selected from the group comprising the ethylene glycol, propylene glycol, polyethylene glycol and polypropylene glycol acrylates and methacrylates, allyl alcohol, allylamine, methallylamine and o-allylphenol.

9. Copolymer according to any one of Claims 1 to 8, characterized in that the

surfactant compound involved in the make-up of the surfactant monomer (c) has the formula



wherein

- the term  $(O - R_2)$  is ethylene oxide, propylene oxide, butylene oxide or a combination of at least two of these oxygenated groups;
- n, which represents the average number of terms present in said surfactant compound, has a value of between 5 and 150;
- the term  $R_1$ , comprising 1 to 32 carbon atoms, is selected from the group consisting of hydrocarbon- and/or amine-containing chemical structures such as aliphatic or cycloaliphatic alkyls, substituted or unsubstituted aryls, polyaryls, secondary amines of formula  $(R_3)(R_4)N$ - wherein  $R_3$  and  $R_4$  are hydrocarbon groups having 1 to 20 carbon atoms.

10. Copolymer according to Claim 9, characterized in that the term  $R_1$  is preferably selected from among  $C_{12}$  to  $C_{30}$  hydrocarbon chains, the  $-O-R_2$  term from among ethylene and/or propylene oxides, and n in the range of 15 to 50.

11. Copolymer according to one of Claims 9 or 10, characterized in that the surfactant compound is preferably selected from the group comprising ethoxylated dilaurylamines, ethoxylated octyl- and nonylphenols, oxyethylated lauryl alcohol, stearyl alcohol, cetyl alcohol, ethoxylated di- and tristerylphenols, taken alone or in a mixture.

12. Copolymer according to any one of Claims 1 to 11, characterized in that it contains, expressed as a percentage by weight,

- a) from 15 to 75 %, preferably 30 to 45 % by weight of ethylenically unsaturated monomer(s) having at least one carboxylic function;
- b) from 25 to 70 %, preferably 45 to 60 % of other ethylenically unsaturated monomer(s) devoid of carboxylic function,

- c) from 0.5 to 35 %, preferably 4 to 15 % of surfactant monomer(s) having at least one urethane function resulting from the reaction of an ethylenically unsaturated isocyanate with a surfactant compound having a hydroxyl function reactive towards the -NCO group.

13. Copolymer according to any one of Claims 1 to 12, characterized in that it is at least partially neutralized.

14. Copolymer according to Claim 13, characterized in that the neutralization agent is preferably lithium hydroxide, sodium hydroxide, potassium hydroxide, ammonium hydroxide, calcium hydroxide, magnesium hydroxide or an amine, taken alone or in combination.

15. Charged and/or pigmented aqueous compositions, characterized in that they contain the copolymer defined in Claims 1 to 14.

16. Charged and/or pigmented aqueous compositions according to Claim 15, characterized in that, white or colored, they contain as principal components an aqueous phase, charges and/or pigments, a natural or synthetic binder, the associative thickening copolymer according to Claims 1 to 14, and possibly, as secondary components, a dispersant, additives as diverse as coalescence agents, biocides, surface-active agents and antifoaming agents.

17. Aqueous compositions according to one or the other of Claims 15 or 16, characterized in that the thickening copolymer is introduced therein in an amount of 0.1 % to 10 %, preferably 0.1 % to 5 %, and very preferably 0.4 % to 1.5 % by dry weight relative to the total weight of said compositions.

18. Application of the thickening copolymer according to any one of Claims 1 to 17 to aqueous coating compositions, aqueous paints, coating slips, printing pastes, leather finishing products, cosmetic compositions, detergents and drilling fluids.

## DOCUMENTS CONSIDERED PERTINENT

	Citation of the document, with indication of the relevant parts, if necessary	Relates to Claim	CLASSIFICATION OF APPLICATION (Int. Cl. 5)
D, A	US-A-4,600,761 (C. G. RUFFNER et al.) -----		C 08 F 220 / 04 C 08 F 8 / 44 C 09 K 7 / 02 C 09 D 7 / 12 A 61 K 7 / 00
D, A	US-A-4,514,552 (G. D. SHAY et al.) -----		
A	EP-A-0 173 109 (DESOTO) -----		

## TECHNICAL AREAS SEARCHED (Int. Cl. 5)

C 08 F

The present report was prepared for all claims

Place of search	Closing date of search	Examiner
THE HAGUE	OCT. 2, 1989	CAUWENBERG, C.L.M.

## CATEGORY OF DOCUMENTS CITED

X: Of particular importance in itself  
Y: Particularly pertinent in combination with another document of the same category  
A: Technological background  
D: Nonwritten disclosure  
P: Interim document

T: Theory or principle on which invention is based  
E: Prior patent, but published on the filing date or after this date  
D: Cited in the application  
L: Cited for other reasons

&: Member of the same family;  
correspondent patent